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Removing Manganese and Chromium from Drinking Water using Tannin-based Biosorbents

Mustafa Hamdan Mahmood

College of Veterinary, University of Diyala, Iraq

mustafa.h.m@uodiyala.edu.iq

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Abstract

Water is a vital source for all aspects of humanity and ecosystem existence. Unique of the greatest commanding ecological problems currently is earth water pollution among the extensive variety of pollutants affecting water incomes, heavy metals raising concerns over their potential effects on human health and the environment, even with small quantity. This study was designed for the synthesis of condensed tannin resin from leaves of the *Acacia nilotica* plant to remove heavy metals manganese and chromium from drinking water samples collected from Alrazi station for drinking water production in Alrazi Street, Baqubah, Iraq. Water sample treatment with condensed tannin resin was taken every ten minutes for a full hour to measure the amount of removing heavy metals. The results showed that condensed tannin resin was the most efficient in removing heavy metals manganese and chromium. The concentration of manganese recorded the following values 0.041, 0.038, 0.034, 0.032, 0.029, and 0.029 respectively, every ten minutes for a full hour with removing rate of 39.6% compared with the value of control sample recorded 0.048, While the concentration of chromium recorded the following values 0.012, 0.010, 0.008, 0.007, 0.005 and 0.005 respectively every ten minutes for a full hour with removing rate 70.6% compared with the value of control sample recorded 0.017. The study of the adsorption kinetics of heavy metals manganese and chromium for both uptake capacity of heavy metal by condensed tannin resin and reach equilibrium was at a fixed time for each

mineral above. The condensed tannin resin extracted from leaves of the *A. nilotica* plant was efficient in removing heavy metals manganese and chromium from drinking water.

Key words: drinking water, tannin, *Acacia nilotica.*

Introduction

Water is a vital source for all aspects of humanity and ecosystem existence [1]. Unique of the greatest commanding ecological problems currently is earth water pollution among the extensive variety of pollutants affecting water incomes. Heavy metals cause specific anxiety due to their robust poisonousness even with little attention [2]. Metals commonly, a density of at least 5 g cm−3 are heavy metallic which is unique of the greatest stubborn contaminants originating in earth water [3]. Different organic contaminants, the main source of heavy metals do not damage and They accumulate as they move through the food chain, creating possible danger to human health threats and environmental stability [3,4]. Certain metals mostly support wildlife on account of corrosion and enduring parental pillars spread into earth water [5]. landfill leachates, municipal and industrial wastewater is an additional cause of metal ion pollution in earth water [5]. Companies such as metallic plating, withdrawal operations, manure compost fertilizer production, paper production, Insecticides, drugs manufacturing etc., direct or indirect release of heavy metal wastewater into the setting. Particularly in third World countries contaminating superficial water and earth water [6,7]. Environmental pollution of heavy metals is increasingly becoming a problem and has become of great concern due to the adverse effects it is causing in both work and in houses [8]. Although small amounts are found in our food and some are essential for physical fitness, large amounts of most of them may cause acute or long-term poisoning [8]. The public dangerous metals that originate in earth water are arsenic (As), iron (Fe), manganese (Mn), mercury (Hg), lead (Pb), chromium (Cr), cadmium (Cd), nickel (Ni), and copper (Cu) [4,9,10]. Manganese is an important metal for human health, being absolutely necessary for development, metabolism, and the antioxidant system. Nevertheless, excessive exposure or intake may lead to a condition known as manganism [11]. Excess concentrations of heavy metal chromium (Cr (VI)) occurring in water and groundwater are very poisonous, cancer-causing, mutagenic, and teratogenic [12,13,14]. Tannins are typically obtained from leaves, bark, seeds, and fruits of several plants [15]. The tannin composites consist a poly-hydroxyphenyl group have a great attraction for heavy metal ions such as Cadmium, Cobalt, Chromium, and Uranium [16]. The objective of the present study is to propose a novel retrieval method for heavy metals manganese and chromium using Tannin-based biosorbents extracted from *A. nilotica* plant leaves.

Materials and Methods

Collection of *A. nilotica* leaves

The leaves of the *A. nilotica* Figure (1) plant were collected from the garden of Diyala University in elastic bags and transported to the workroom straight. They were washed with tap water, and then with distilled water to remove filth, dust, and superficial pollution. The leaves were left to dehydrate in a workroom for one week. The dry form of leaves was crushed in an electrical grinder until converted into powder.

Figure 1: Leaves of *A. nilotica*.

Tannin resin extracts

An amount of 300 grams of *A. nilotica* leaf powder was washed with tap water and positioned in a conical flask containing 1800 ml of distilled water Figure (2). An amount of 1.5 grams of sodium hydroxide (NaOH) grains was added to the conical flask and mixed in a hot plate stirrer at 90 ºC for one hour. The brownish-dark slurry was filtrated through Whatman No.1 in a porcelain funnel under a vacuum. The solids were reduced and discarded and the filtrate was collected and then dried in a vacuum oven at 60 ºC for 24 hours. Dry tannin resin (TR) was collected and stored in sealed packages [17]. The procedure was repeated on a great scale to collect a large amount of dry tannin resin powder.

Figure 2: Extraction of condensed tannin resin.

Preparation of condensed tannin resin

The method of [17] was used to prepare TR gel.

A quantity of 150 grams of tannin resin was dissolved in 250ml of NaOH (0.5%) on the hot magnetic stirrer at 80 ° C for 30 minutes and mixed continuously at 80 ° C for one hour. After that, 48ml of formalin (37%) was added and left to stand for two hours at the same temperature. The mixture was then transferred to the vacuum oven at 60 ° C for 24 hours. The dry gel was crushed and ground by an electric motor and collected in a clean beaker. The continents were washed with dH_2O several times, left for 30 minutes, and then the water was discarded. The deposit was washed with nitric acid (1M) and then washed with dH_2O. The process was repeated twice and the water was discarded, then dried in a vacuum dryer for 24 hours.

Check of solubility of condensed tannin resin in water

Five grams of condensed tannin resin were added to glasses covering 25ml tap water and deionized water individually. Dissolving capability was checked for one hour.

Water sampling

Water samples were collected from Alrazi station for drinking water production in Alrazi Street, Baqubah, Iraq. The point of water sampling was determined from the stream of the sand filtration stage before the chlorination stage. The samples were collected in screw-cupped plastic containers with a 20 L capacity and transferred directly to the laboratory.

Mineral determination

Two heavy metals were measured in the water samples, these are manganese and chromium.

Field experiments: Prepared condensed tannin resin was examined for its ability to reduce heavy metals manganese and chromium from water samples collected from the sand filtration stage in selected line Alrazi station.

The test steps included the following:

1- Clean and anti-acid 5L plastic containers with lids were used for the treatment of water supplied directly from the stream of the sand filtration stage.

2- five liters of water were added to the container.

3- A quantity of 10gm of condensed tannin resin was added to the container.

4- The contents of the container were mixed vigorously for 5min and the contents were left to settle.

5- Samples were collected every 10 minutes for an entire hour to conduct heavy metals tests.

6- Experiments were done in duplicate for treatment.

7- The control treatment represents a sample of water without any addition.

Equilibrium analysis

From the initial and final concentrations, percentage removal can be calculated by the following formula:

Heavy metal removing % $= \frac{C_0 - C_f}{C_o}$ X 100% …….. [12].

Where C_0 is the initial concentration of ions in mg/L and C_f is the final concentration of ions in mg/L. The results obtained in the batch mode were used to calculate the equilibrium metal uptake capacity. The amounts of pollutants uptake by condensed tannin resin at the equilibrium (q_e) were calculated by the following mass-balance relationship:

$$q_e = \frac{V(C_O - C_F)}{W}$$ ……. [13].

Where q_e is the equilibrium uptake capacity in mg/g, V is the sample volume in liters, C_0 is the initial metal ion concentration in mg/L, C_F the equilibrium metal ion concentration in mg/L, and W is the dry weight of adsorbent in grams.

Results

Solubility in water

The solubility of the prepared condensed tannin resin was tested in tap water and dH_2O. The mixtures were left in tap water and deionized water for a full hour. The results of the tests showed that the condensed tannin resin did not dissolve in tap water or deionized water. [18] Showed that the tannin resin extracted from *A. nilotica* by this method was insoluble in water especially after polymerized by formalin, and thus the possibility of using it in the adsorption and recovery of heavy metals.

Treatment of water sample with condensed tannin resin

Table 1: Analysis of treated water with condensed tannin resin.

Parameter with unit	WHO Standard	Control treatment	Time/min						Removing (%)
			10	20	30	40	50	60	
Manganese mg/L	0.2	0.048	0.041	0.038	0.034	0.032	0.029	0.029	39.6
Chromium mg/L	0.05	0.017	0.012	0.010	0.008	0.007	0.005	0.005	70.6

The results of the analysis of water treatments with condensed tannin resin show that the concentrations of heavy metals are greatly fewer than the allowable limits in all specifications. However, notwithstanding that, the ratio of removing heavy metals using condensed tannin resin is significant and is considered an indicator of the competence of the condensed tannin resin in removing heavy metals if they exist in higher concentrations.

Heavy metals removing

The results showed that the condensed tannin resin has a high affinity for heavy metals manganese and chromium with removal rates of 39.6% and 70.6% after 50min respectively, as the equilibrium uptake capacity, which was reached after 50min, and the value did not change after a full hour. The removal rate and adsorption isotherm equilibrium were reached a balance during the first 50 minutes of the reaction and the value did not change after a full hour, these dependent on the concentration of adsorbent and heavy metals in a water sample. The previous study by [6] showed the whole adsorption of all Hg with steadying by using tannin resin for

10minutes. Initially, all adsorbent seats were unfilled and the solute concentration was high, so the real removal of heavy metals was high, subsequently, an actual slight decrease in the heavy metal uptake by condensed tannin resin because there are few superficial active sites on condensed tannin resin. After these values, it is suggested that only the slightest time is necessary for the adsorption of heavy metal ions by condensed tannin resin prepared by *A. nilotica* leaves [19]. The activity of condensed tannin resin in the adsorption of heavy metals manganese and chromium because the tannin resin containing a poly-hydroxyphenyl group has an excessive attraction for heavy metal ions [20].

Table 2: Removal rate of manganese and chromium with time.

Time/minute	Removal rate % for manganese	Removal rate % for chromium
10	14.6	29.4
20	20.8	41.2
30	29.2	52.9
40	33.3	58.8
50	39.6	70.6
60	39.6	70.6

Table two shows that the removal rate for manganese and chromium increased with time during the first 50 min because more active site on condensed tannin resin after this time the adsorbent seats were filled and reached equilibrium [20] as shown in figures three and four.

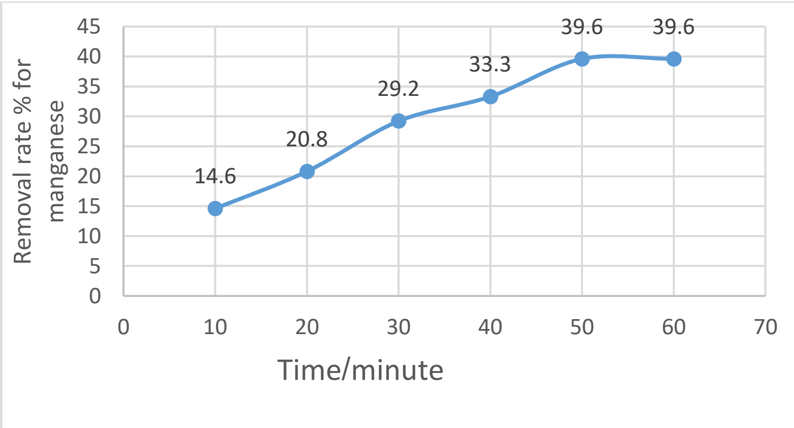

Figure 3: Removal rate of manganese with time.

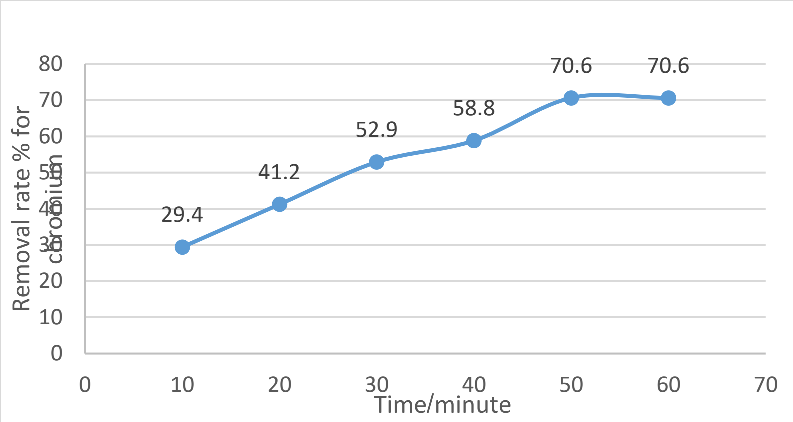

Figure 4: Removal rate of chromium with time.

Table 3: The equilibrium uptake capacity in mg/g for manganese and chromium with time.

Time /minute	q_e mg/g for manganese	q_e mg/g for chromium
10	0.0035	0.0025
20	0.005	0.0035
30	0.007	0.0045
40	0.008	0.005
50	0.0095	0.006
60	0.0095	0.006

Table (3) shows adsorption isotherm equilibrium reached the balance during the first 50 of the reaction and the value did not change after a full hour, these are dependent on the concentration of adsorbent and heavy metals in a water sample. During the first 50 minutes more active site abundant unfilled on condensed tannin resin. After this time whole active site was filled and the adsorption isotherm equilibrium reached the balance as shown in Figures five and six [20].

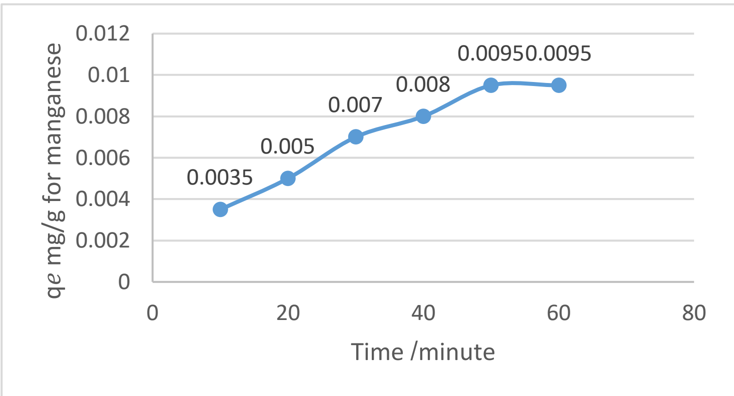

Figure 5: The equilibrium uptake capacity in mg/g for manganese time.

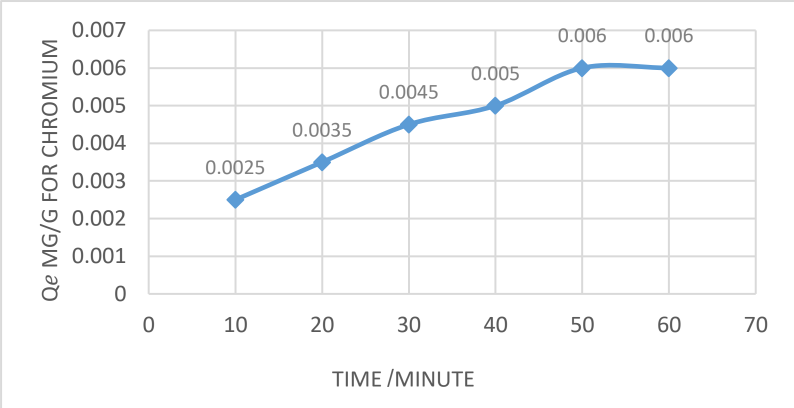

Figure 6: The equilibrium uptake capacity in mg/g for chromium with time.

Conclusions

Tannin resin extracted from leaves of *A. nilotica* plant was efficient in removing heavy metals manganese and chromium from drinking water. Condensed tannin resin is easy to extract, efficient, non-toxic, non-expensive, and can be used several times by washing with nitric acid.

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